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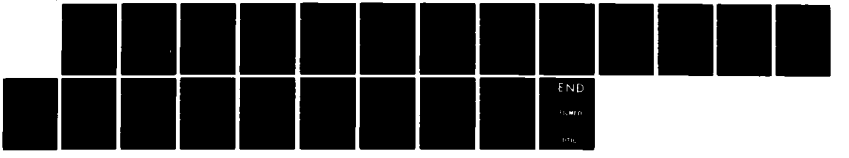

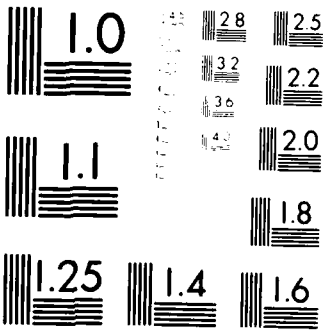

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Polyboron Spiro-Cations Based on Bridging Dipyrazol-1-ylboryl Units

by

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Syntheses are described for polyboron spiro-cations of the types $[R_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2BR'_2]^+$ (pz = pyrazolyl = $N_2C_3H_3$; R = R' = H, R = H and R' = C_2H_5, R = R' = C_2H_5) and $[R_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2BR_2]^{2+}$ (R = H, C_2H_5), which

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were obtained by reaction of B-(pyrazol-1'-yl)pyrazaboles with $(CH_3)_3NBH_2I$ or $(C_2H_5)_2BOts$ (ts = tosyl), respectively. In addition, an intermediate species containing both terminal and bridging pyrazolyl groups, i.e., $[(CH_3)_3NBH_2(\mu\text{-pz})B(pz)(\mu\text{-pz})_2B(pz)(\mu\text{-pz})BH_2N(CH_3)_3]^{2+}$, was identified and characterized. NMR data of the various species are reported; specific assignments of ^1H and ^{13}C signals to individual pyrazolyl groups were made on the basis of HOMCOR and HETCOR 2D NMR studies.

Contribution from the Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506; and the Polymer Products Department, E. I. DuPont de Nemours & Co., Parkersburg, West Virginia 26101

Polyboron Spiro-Cations Based on Bridging Dipyrazolylboryl Units[1]

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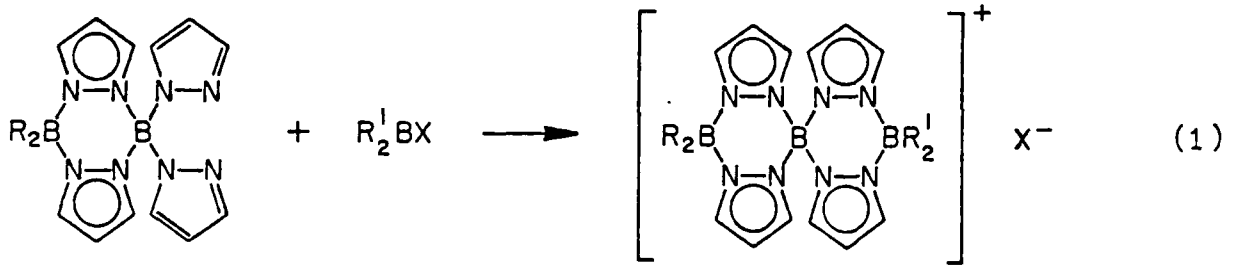
Received.....

Syntheses are described for polyboron spiro-cations of the types $[R_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2BR'_2]^+$ (pz = pyrazolyl = $N_2C_3H_3$; R = R' = H, R = H and R' = C_2H_5, R = R' = C_2H_5) and $[R_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2BR_2]^{2+}$ (R = H, C_2H_5), which were obtained by reaction of B-(pyrazol-1'-yl)pyrazaboles with $(CH_3)_3NBH_2I$ or $(C_2H_5)_2BOts$ (ts = tosyl), respectively. In addition, an intermediate species containing both terminal and bridging pyrazolyl groups, i.e., $[(CH_3)_3NBH_2(\mu\text{-pz})B(pz)(\mu\text{-pz})_2B(pz)(\mu\text{-pz})BH_2N(CH_3)_3]^{2+}$, was identified and characterized. NMR data of the various species are reported ; specific assignments of ^1H and ^{13}C signals to individual pyrazolyl groups were made on the basis of HOMCOR and HETCOR 2D NMR studies.

Introduction

The ability of poly(pyrazol-1-yl)borate ions, $[B(pz)_{4-n}R_n]^-$ (pz = pyrazolyl = $N_2C_3H_3$, R = non-coordinating ligand, n = 0-2), to act as uninegative polydentate ligands has been well established and numerous metal complexes employing poly(pyrazol-1-yl)borate groups have been described.[2] The terminal pyrazolyl groups of (the neutral) B-(pyrazol-1'-yl)pyrazaboles should also exhibit coordinating ability. Indeed, a brief note reports the interaction of 4,4-diethyl-8,8-di(pyrazol-1'-yl)pyrazabole, $(C_2H_5)_2B(\mu\text{-}pz)_2B(pz)_2$, and of 4,4,8,8-tetrakis(pyrazol-1'-yl)-pyrazabole, $(pz)_2B(\mu\text{-}pz)_2B(pz)_2$, with $(C_2H_5)_2BOts$ (ts = tosyl) or π-allylpalladium chloride dimer but little experimental details were given.[3] The present study describes the interaction of B-(pyrazol-1'-yl)pyrazaboles with boranes containing a ready leaving group according to the general eq 1.



(1)

Thus, the basic reaction involves the conversion of two boron-bonded terminal pyrazolyl groups into units that bridge to an additional boron atom; the latter then carries a formal +1 charge.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY; all compounds gave satisfactory data. Melting points (uncorr.) were determined on a Mel-Temp block.

NMR spectra were recorded on a Varian XL-200 instrument. Chemical shift data are given in ppm with positive values indicating downfield from the reference (internal Me_4Si for ^1H and ^{13}C, external Et_2OBF_3 for ^{11}B); s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, m = unresolved multiplet and an asterisk denotes a broad signal. Coupling constants J are given in Hz. Details for HOMCOR and HETCOR 2D NMR experiments have been described elsewhere.[4]

$[H_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2BH_2]^+PF_6^-$. A solution of 1.99 g (10 mmole) of trimethylamine-monoiodoborane[5] in 150 mL mesitylene was added to a solution of 2.92 g (10 mmole) of 4,4-di(pyrazol-1'-yl)-pyrazabole[6] in 25 mL of toluene. The stirred mixture was slowly warmed to reflux over a period of 6 h and reflux was then maintained for 25 h. After cooling to room temperature, the precipitate was collected, washed with toluene and then with petroleum ether and dried in vacuum. The crude product (3.6 g) was dissolved in 30 mL of water and a small amount of insoluble material was filtered off. A concentrated aqueous solution of ammonium hexafluorophosphate was added to the clear filtrate until no further precipitate formed. The precipitate was collected, washed with water and dried to give 2.4 g (53 %)

of the desired material, which starts shrinking near 150 °C and melts (with decomposition) at 165-168 °C.

NMR data (solution in CD_3CN): $\delta(^1H)$ = 8.18 (1 H, unresolved d), 7.73 (1 H, d, J = 2.4), 6.72 (1 H, t, J = 2.2), ca. 3.5* (1 H); $\delta(^{11}B)$ = -1.3 (1 B), -7.7* (2 B, sharpens in proton decoupled spectrum); $\delta(^{13}C)$ (proton decoupled) = 141.1, 139.3, 110.3.

$\underline{[H_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2B(C_2H_5)_2]^+PF_6^-}$. To a solution of 2.92 g (10 mmole) of 4,4-di(pyrazol-1'-yl)pyrazabole[6] in 100 mL of toluene was added slightly more than 2 molar equivalents of a standard solution of diethylboryl tosylate[7] in toluene. The mixture was refluxed for 2 h. On cooling, a viscous oil settled and the toluene was decanted. The oil was shaken briefly with three 25-mL portions of toluene and then dissolved in 25 mL of water. After filtration, a concentrated aqueous solution of ammonium hexafluorophosphate was added to the clear filtrate until no further precipitate was formed. The precipitate was collected, washed with water and dried to give 2.2 g (43.5 %) of the title compound, mp 168-171 °C (with decomposition).

NMR data (solution in CD_3CN): $\delta(^1H)$ = 8.23 (1 H, unresolved d), 8.18 (1 H, unresolved d), 7.94 (1 H, unresolved d), 7.41 (1 H, unresolved d), 6.84 (1 H, ill-resolved t, J ca. 2.2), 6.70 (1 H, ill-resolved t, J ca. 2.6), ca. 3.4* (1 H), 0.86 (2 H, q, J ca. 7.3), 0.59 (3 H, t, J ca. 7.5); $\delta(^{11}B)$ = +5.2* (1 B), -1.5 (1 B), -7.5* (1 B, sharpens in proton decoupled spectrum).

$\underline{[(C_2H_5)_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2B(C_2H_5)_2]^+PF_6^-}$. To a solution of 3.48 g (10 mmole) of 4,4-diethyl-8,8-di(pyrazol-1'-yl)pyrazabole[7] in 100 mL of toluene was added, with stirring, 10 mL of a 1.0 M solution of diethylboryl tosylate[7] in toluene. The resultant precipitate was collected and dissolved in a minimum quantity of hot water. The title compound was precipitated by adding an excess of aqueous ammonium hexafluorophosphate solution. The crude product was collected and was purified by dissolving in a minimum quantity of hot acetonitrile, filtering the hot solution and adding ethyl acetate to a cloud point. On cooling, 3.5 g (62 %) of the crystalline salt, mp 220-223 °C, were obtained.

Alternate procedure. A mixture of 3.2 g of potassium tetrakis(pyrazol-1'-yl)borate and 200 mL of a 0.4 M solution of diethylboryl tosylate in toluene was refluxed with stirring for 3 h. After cooling to room temperature, the clear toluene solution was decanted to leave an oily residue, which crystallized after being covered and shaken with 30 mL of water. The solid material was collected, washed with ether and dried to give 2.95 g (50.2 %) of the tosylate salt of the title cation. It was purified by dissolving in acetonitrile and precipitating with ether, mp 212-215 °C.

NMR data (solution in DMSO-d_6): $\delta(^1H)$ = 8.63 (4 H, d, J = 2.2), 7.64 (4 H, d, J = 2.6), 7.52 (2 H, d. J = 8), 7.12 (2 H, d, J = 8), 7.01 (4 H, t, J = 2.5), 2.29 (3 H, s), 0.87 (8 H, q, J = 7), 0.61 (10 H, t, J = 7); $\delta(^{11}B)$ = +4.7* (2 B), -2.2 (1 B, $h_{\frac{1}{2}}$ = 25 Hz).

The tosylate salt was converted to the hexafluorophosphate salt by suspending the former in an aqueous solution of 2.5 g of ammonium hexafluorophosphate and stirring the mixture for 3 h at room temperature. The solid material was collected, dissolved in acetonitrile and precipitated with water to give a pure material, mp 217-221 °C. An analytical sample had a mp 225-226 °C.

NMR data (solution in CD_3CN): $\delta(^1H)$ = 8.24 (1 H, unresolved d), 7.52 (1 H, unresolved d), 6.81 (1 H, ill-resolved t, J ca. 2.5), 0.89 (2 H, q, J ca. 7.6), 0.65 (3 H, t, J ca. 7.5); $\delta(^{11}B)$ = +5.1* (2 B), -1.8 (1 B); $\delta(^{13}C)$ (proton decoupled) = 140.9, 138.4, 112.1, ca. 18*, 9.4.

$\underline{[H_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2BH_2]^{2+}2PF_6^-}$. A mixture of 6.4 g (15 mmole) of 4,4,8,8-tetrakis(pyrazol-1'-yl)pyrazabole,[8] 6.5 g (33 mmole) of trimethylamine-monoiodoborane[5] and 125 mL of mesitylene was heated with stirring for 6 h in an oil-bath of 60 °C, another 8 h at 90 °C, and finally refluxed for 6 h. After cooling to room temperature, the insoluble material was collected, washed with benzene and dried. It was dissolved in water and a small amount of insoluble material was filtered off. A solution of 6 g of ammonium hexafluorophosphate in water was added and the mixture was stirred for 15 min. The precipitate was collected, washed with water and dried to give 9.5 g (86 %) of crude product, mp 210-212 °C (with decomposition). It was purified by dissolving in a minimum quantity of acetonitrile and adding a large excess

of ethyl acetate. The resultant precipitate was collected, washed with ethyl acetate and dried under vacuum to give 6.9 g (62 %) of a material, mp 220-224 °C (with decomposition). An analytical sample had a mp 224-228 °C (with decomposition).

NMR data (solution in CD_3CN): $\delta(^1H)$ = 8.37 (2 H, d, J = 2.9), 8.28 (2 H, d, J = 2.2), 7.64 (2 H, d, J = 2.9), 7.04 (1 H, t, J = 2.8), 6.75 (2 H, t, J = 2.6), ca. 3.4* (2 H); $\delta(^{11}B)$ = -1.5 (1 B), -7.5* (1 B, sharpens in proton decoupled spectrum); $\delta(^{13}C)$ (proton decoupled) = 145.2, 142.5, 139.2, 114.6, 111.2.

$\underline{[(C_2H_5)_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2B(C_2H_5)_2]^{2+}2PF_6^-}$. Twenty mL of a 1.0 M solution of diethylboryl tosylate in toluene was added with stirring to a solution of 4.24 g (10 mmole) of 4,4,8,8-tetrakis(pyrazol-1'-yl)pyrazabole[8] in 250 mL of hot toluene and the mixture was refluxed for 30 min. After cooling to room temperature, 8.3 g (90 %) of colorless crystals of the tosylate salt were collected. They were converted to the corresponding hexafluorophosphate salt by dissolving the tosylate in dimethylformamide/water (10:1 by volume) and addition of excess aqueous ammonium hexafluorophosphate solution. The resultant precipitate was purified by dissolving in hot acetonitrile, filtering while hot, and adding ethyl acetate to a cloud point. On cooling, 5.8 g (68 %) of crystalline material, decomposing at 332-334 °C (by DSC), were obtained.

NMR data: solution in CD_3CN, $\delta(^1H)$ = 8.35 (2 H, d, J = 2.2), 7.99 (2 H, d, J = 2.5), 7.71 (2 H, d, J = 2.9), 7.00 (1 H, t, J = 2.7), 6.94 (2 H, t, J = 2.7), 0.9 (4 H, unresolved m), 0.7

(6 H, unresolved m); $\delta(^{11}B)$ = +6.5 (1 B, $h_{\frac{1}{2}}$ = 300 Hz), -1.5 (1 B, $h_{\frac{1}{2}}$ = 20 Hz); $\delta(^{13}C)$ (proton decoupled) = 144.7, 144.4, 142.3, 142.1, 139.3, 139.0, 115.3, 112.4, 18.1*, 9.1; solution in DMSO-d_6: $\delta(^{1}H)$ = 8.70 (2 H, d, J = 2.2), 8.20 (2 H, d, J = 2.7), 8.17 (2 H, d, J = 2.9), 7.18 (1 H, t, J = 2.7), 7.08 (2 H, t, J = 2.6), 0.9 (4 H, m), 0.65 (6 H, m); $\delta(^{11}B)$ = ca. +6*, -2.0 ($h_{\frac{1}{2}}$ = 50 Hz); $\delta(^{13}C)$ (proton decoupled) = 143.3, 141.1, 138.6, 114.2, 111.0, 16.7*, 8.6.

Results and Discussion

The interaction of nitrogen bases with trimethylamine-monoiodoborane can lead to both iodide ion and base displacement according to eq 2.[9]

$$(CH_3)_3NBH_2I + 2\ L \longrightarrow (CH_3)_3N + [L_2BH_2]^+I^- \qquad (2)$$

On that basis, the reaction of 4,4-di(pyrazol-1'-yl)pyrazabole with trimethylamine-monoiodoborane could proceed as follows:

$$(CH_3)_3NBH_2I + (pz)_2B(\mu\text{-}pz)_2BH_2 \longrightarrow (CH_3)_3N + [H_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2BH_2]^+I^- \qquad (3)$$

Indeed, reaction according to eq 3 can be realized and the cation $[H_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2BH_2]^+$ was isolated as its hexafluorophosphate salt. However, the reaction requires extreme care if somewhat reasonable yields of product are desired. First of all, the reaction temperature should only gradually be increased, apparently in order to avoid decomposition of yet unreacted $(CH_3)_3NBH_2I$. Secondly, sufficiently long reaction times at

fairly high temperatures are required to remove at least most of the trimethylamine from an intermediate product.

The overall process seems to involve at least two steps. Initially, iodide ion displacement occurs to give the intermediate $[H_2B(\mu\text{-}pz)_2B(pz)(\mu\text{-}pz)BH_2N(CH_3)_3]^+I^-$. This process is fairly slow at room temperature but proceeds more readily at 50-70 °C. In the second phase of the reaction trimethylamine is displaced by the N2 atom of the lone terminal (i.e., non-bridging) pyrazolyl group to give the desired cation $[H_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2BH_2]^+$. This second step is much more sluggish and requires prolonged heating at relatively high temperatures. (Note: A similar two-step mechanism has been postulated for the hydrolysis of $(CH_3)_3NBH_2I$.[10])

The pure salt $[H_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2BH_2]^+PF_6^-$ was isolated from aqueous solution. A HETCOR 2D NMR experiment showed that the signal pairs $\delta(^1H)/\delta(^{13}C)$ = 8.18/141.1, 7.73/139.2 and 6.72/110.3 ppm belong to the individual CH groups of the bridging pyrazolyl moieties.

In order to test the above mechanistic assumptions, the interaction of 4,4,8,8-tetrakis(pyrazol-1'-yl)pyrazabole, $(pz)_2B(\mu\text{-}pz)_2B(pz)_2$, with two molar equivalents of $(CH_3)_3NBH_2I$ was studied in more detail. The stepwise progress of the reaction could be observed by ^{11}B NMR spectroscopy. When a solution of the two cited reagents was stirred at room temperature for several hours, the ^{11}B NMR signals (solution in $CDCl_3$) of $(CH_3)_3NBH_2I$ ($\delta(^{11}B)$ = -9.6 ppm) and of

$(pz)_2B(\mu\text{-}pz)_2B(pz)_2$ ($\delta(^{11}B)$ = -0.1 ppm) still dominated the spectrum. However, two minor signals, $\delta(^{11}B)$ = -1.9 and +4.0 ppm, respectively, were also apparent. These latter became the major signals (and were in 1:1 area ratio) after refluxing the reaction mixture in benzene for 10 h. At this time, the signal for $(CH_3)_3NBH_2I$ was no longer observed and only a minor signal $\delta(^{11}B)$ = -0.1 ppm was still present.

Based on ^1H and ^{13}C NMR data (solution in DMSO-d_6), the primary product at this stage was identified as the salt $[(CH_3)_3NBH_2(\mu\text{-}pz)B(pz)(\mu\text{-}pz)_2B(pz)(\mu\text{-}pz)BH_2N(CH_3)_3]^{2+}2I^-$. The following $\delta(^1H)/\delta(^{13}C)$ signals were observed and were assigned on the basis of fine structure as well as HOMCOR and HETCOR 2D NMR experiments: 7.76(1 H, d)/142.6, 7.37(1 H, d)/137.2 and 6.42(1 H, 2 overlapping d)/107.0 ppm for the two terminal (= non-bridging) pyrazolyl groups; and the sets 8.55(1 H, d)/140.6, 7.24(1 H, d)/134.0 and 6.74(1H, t)/109.5 ppm as well as 8.41(1 H, d)/141.2, 8.18(1 H, d)/142.4 and 7.04(1 H, t)/110.9 ppm for the two different types of bridging (= μ-pz) pyrazolyl groups. The boron-bonded hydrogen was evidenced by a very broad signal near 3.4 ppm; the CH_3 groups exhibited a signal at signal at $\delta(^1H)$ = 2.80 ppm; $\delta(^{13}C)$ = 51.9 ppm.

The ion $[(CH_3)_3NBH_2(\mu\text{-}pz)B(pz)(\mu\text{-}pz)_2B(pz)(\mu\text{-}pz)BH_2N(CH_3)_3]^{2+}$ loses trimethylamine only on prolonged heating in mixture with toluene or, even better, mesitylene. The progress of the reaction can be seen by a continuous decrease in the intenstity of the ^1H NMR signal of the trimethylamine. However, some residual trimethylamine always remains in the crude product

though, ultimately, the salt $[H_2B(\mu\text{-pz})_2(\mu\text{-pz})_2B(\mu\text{-pz})_2BH_2]^{2+}2I^-$ is formed. A HOMCOR 2D NMR experiment (in DMSO-d_6) showed that the observed signals $\delta(^1H)$ = 8.67(2 H, d) and 7.20(1 H, t) ppm, respectively, belong together and must be assigned to the central bridging pyrazolyl groups; and the set $\delta(^1H)$ = 8.21 (2 H, d), 8.20(2 H, d) and 6.87(2 H, t) ppm is then readily assigned to the remaining pyrazolyl groups of the ion. The boron-bonded protons were observed as a very broad signal near $\delta(^1H)$ = 3.9 ppm. In addition, various minor impurity signals and a reasonably strong signal for trimethylamine groups were observed. However, a pure material could be obtained by precipitation of the cation from aqueous solution as the hexafluorophosphate salt, which was further characterized.

Based on HOMCOR and HETCOR 2D NMR experiments, the $\delta(^1H)/\delta(^{13}C)$ signal pairs of $[H_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2BH_2]^{2+}$ (solution in CD_3CN) at 8.37/145.2 and 7.04/114.6 ppm were assigned to the central pyrazolyl groups; and the sets 8.28/142.5, 7.64/139.2 and 6.75/111.2 ppm to the second type of bridging pyrazolyl groups.

Whereas the reaction of terminal Bpz_2 groups of B-(pyrazol-1'-yl)pyrazaboles with $(CH_3)_3NBH_2I$ progressed in stepwise fashion, the interaction of the former with $(C_2H_5)_2BOts$ (ts = tosyl) was straightforward and rapid.[3] Of course, the boron atom in the latter reagent is only in trigonal environment and, hence, coordinates readily with the N2 atom of a terminal boron-bonded pyrazolyl group. In addition, the tosylate group

appears to be an even better leaving moiety than the iodide ion. Finally, the tedious trimethylamine displacement is not required in this case. Thus, the reaction of $(pz)_2B(\mu\text{-}pz)_2B(pz)_2$ with $(C_2H_5)_2BOts$ proceeded readily to yield the desired cation $[(C_2H_5)_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2B(C_2H_5)_2]^{2+}$, which was previously isolated as the hexafluorophosphate salt[3] and was now characterized by NMR data.

The NMR data of the latter species were again assigned on the basis of fine structure as well as HOMCOR and HETCOR 2D NMR experiments (solution in DMSO-d_6) as follows: $\delta(^1H)/\delta(^{13}C)$ = 8.20/143.3 and 7.18/114.2 ppm to the central bridging pyrazolyl groups; and the signals 8.70/141.1, 8.17/138.6 and 7.08/111.0 ppm to the pyrazolyl groups bridging the unsymmetrically substituted boron atoms to the central unit. In CD_3CN (but not in DMSO-d_6) the two types of boron atoms in different encironments are not only clearly seen with $\delta(^{11}B)$ = +6.5 and -1.5 ppm, respectively, but the line shape clearly mandates assignment of the latter signal to the boron atoms in the symmetrical environment, i.e., the central ones. In DMSO-d_6, however, the NMR signal of the boron atoms in the unsymmetrical environment can hardly be recognized.

In this conjunction it is of interest to note that the ^{13}C NMR signals of the N-bonded CH units of the pyrazolyl groups in $[(C_2H_5)_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2B(\mu\text{-}pz)_2B(C_2H_5)_2]^{2+}$ are split in CD_3CN solution (at 22 °C) but not in DMSO-d_6. The signals merge rapidly, however, with even minor increases in temperature. This observation suggests the existence of conformational isomers.

The formation of such polyboron spiro species would ideally give cause to a linear structure with planar B_2N_4 rings. On the other hand, angle considerations for the bonds about boron would tend to favor the B_2N_4 rings to exist in boat conformation. An evaluation of the molecular structures of a series of pyrazaboles as determined by X-ray diffraction has shown that the B_2N_4 ring of these compounds can exist in planar, chair or boat conformation, of which the latter predominates.[11] However, energy differences between the various conformations are very small and packing effects seem to be the major factor governing the conformation of a specific species in the solid state.

In analogy to the above reaction, interaction of $(C_2H_5)_2B(\mu\text{-pz})_2B(pz)_2$ with one molar equivalent of $(C_2H_5)_2BOts$ gave the expected monocation $[(C_2H_5)_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2B(C_2H_5)_2]^+$, which again was isolated as the hexafluorophosphate salt.[3] This latter species has now also been characterized by NMR data (see Experimental Section). Based on a HETCOR 2D NMR experiment, the signal pairs $\delta(^1H)/\delta(^{13}C)$ = 8.24/140.9, 7.52/138.4 and 6.81/112.1 ppm, respectively, belong to individual CH units of the pyrazolyl rings.

The same ion $[(C_2H_5)_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2B(C_2H_5)_2]^+$ was also obtained in a one-step procedure originating from $K[B(pz)_4]$ and two molar equivalents of $(C_2H_5)_2BOts$. However, the yield of this latter reaction was noticeably lower than in the case when a pyrazabole was used as starting material.

Furthermore, the reaction of $(pz)_2B(\mu\text{-pz})_2BH_2$ with $(C_2H_5)_2BOts$ was employed to form the unsymmetrical cation

$[(C_2H_5)_2B(\mu\text{-pz})_2B(\mu\text{-pz})_2BH_2]^+$, in which the two terminal boron atoms are in non-equivalent environment. This is readily apparent from the ^{11}B NMR spectral data (see Experimental Section).

The NMR spectral data of the various cations show some noteworthy trends. Individual positions of the three monocations are labelled in 1 and relevant ^1H and ^{11}B NMR data are summarized in Table I. The suggested assignments of $H^3(H^4)$ versus $H^1(H^6)$ are based on the assumption that chemical shift data for the former should be much less affected by the nature of R and R' than the latter.

Similarly, individual positions of the two dications are labelled in 2 and relevant $\delta(^1H)/\delta(^{13}C)$ and $\delta(^{11}B)$ data are listed in Table II. ($\delta(^{13}C)$ signals for positions 1, 3 and 4 for R = C_2H_5 are averaged for the two distinct signals that are observed for each in CD_3CN solution.)

The ^1H and ^{11}B chemical shift data for the two sets of cations appear to correlate well. The one surprising feature is the fact that for 2 with R = C_2H_5, the most downfield ^{13}C signal does not go with the most downfield ^1H signal.

The yields of the various salts as described in the preceding are not always satisfactory. Admittedly, no serious effort has yet been made to improve on yields. However, in view of recent findings that - in contrast to earlier assumptions[12] - the pyrazabole ring can indeed open during chemical manipulations,[13] more basic studies on the chemistry

of pyrazaboles are needed in order to influence the progress of desired processes and limit side-reactions.

In any case, the present data clearly suggest that even larger cations of this same type with the general formula $[R_2B(\mu\text{-pz})_2\{B(\mu\text{-pz})_2\}_nBR_2]^{n+}$ should be accessible: terminal R substituents of a structural unit $(\mu\text{-pz})_2BR_2$ have been replaced by halogen[12,14] which, in turn, was replaced by pyrazolyl groups,[13] thus providing a site for further chain elongation.

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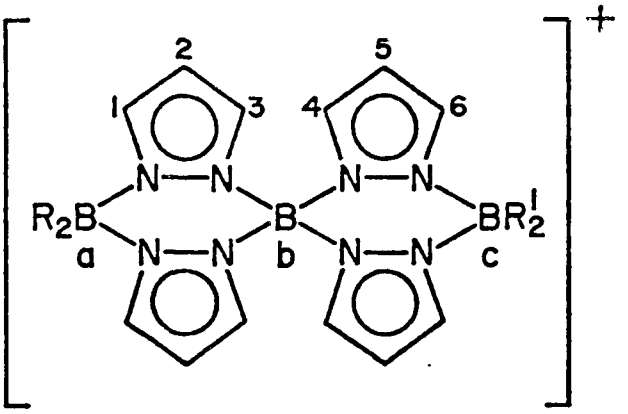
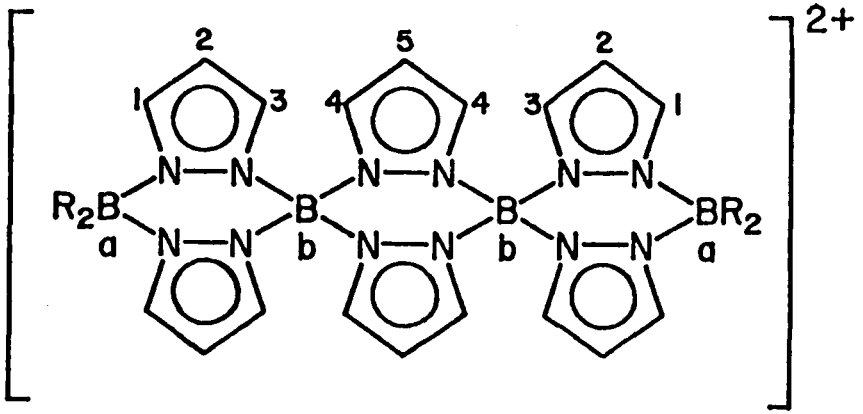
Table I. Survey of Selected Chemical Shift Data of Spiro-Cations of Type 1.



1

compound	$\delta(^1H)$ (in ppm) of position 1(6)	2(5)	3(4)
R = R' = H	7.73	6.72	8.18
R = H, R' = C_2H_5	7.94(7.52)	6.81(6.84)	8.18(8.23)
R = R' = C_2H_5	7.52	6.81	8.24
	$\delta(^{11}B)$ (in ppm) of B^a	B^b	B^c
R = R' = H	-7.7	-1.3	-7.7
R = H, R' = C_2H_5	-7.5	-1.5	+5.2
R = R' = C_2H_5	+5.1	-1.8	+5.1

Table II. Survey of Selected Chemical Shift Data of Spiro-Cations of Type 2.



2

compound	$\delta(^1H)/\delta(^{13}C)$ (in ppm) of position 1	2	3	4	5
R = H	7.64/139.2	6.75/111.2	8.28/142.5	8.37/145.2	7.04/114.6
R = C_2H_5	7.71/139.1	6.94/112.4	8.35/142.2	7.99/144.4	7.00/115.3

	$\delta(^{11}B)$ (in ppm) of B^a	B^b
R = H	-7.5	-1.5
R = C_2H_5	+6.5	-1.5

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